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(54) **POLYETHYLENE IMINE BASED DENDRITIC DISPERSANT**

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CPC ***B01F 17/005*** (2013.01); ***B01J 13/0034*** (2013.01); ***C09B 67/0085*** (2013.01); ***C09C 3/08*** (2013.01); ***C09D 7/02*** (2013.01)

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CPC B01F 17/005; B01J 13/0034; C09D 7/02; C09C 3/08; C09B 67/0085
USPC 516/203; 525/450, 540, 901; 526/910
See application file for complete search history.

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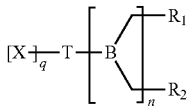
(57) **ABSTRACT**

The present disclosure relates to a liquid dispersant of the formula I



I

wherein

T is selected from a polyethylene imine (PEI) or modified PEI moiety, polyvinylamine (PVA) or modified PVA, or polyallylamine (PAA) or modified PAA;

B is a branched monomer;

R_1 and R_2 independently of one another are hydrophobic groups;

X is B with —OH terminal group, or R_1 or R_2,

q is a number between 5-2000, with the proviso that q is less than the sum of all amine groups of PEI, PVA, PAA; and

n is a number of 1-6.

9 Claims, No Drawings

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POLYETHYLENE IMINE BASED DENDRITIC DISPERSANT

The invention relates to a liquid dispersant based on polar polyamines characterized by a "dendritic" structure.

WO94/21368 describes a dispersant comprising a polyethylene imine residue carrying polyester chains derived from a caprolactone and at least one other specified lactone or hydroxycarboxylic acid.

U.S. Pat. No. 6,583,213 or WO99/55763 (Avecia) describes an amine dispersant with polyester chains attached to an amino or imino group of the amine via an ethylenically unsaturated end group of the polyester. It describes an amine dispersant containing one or more amino and/or imino groups, a poly(oxy-C1-6-alkylene carbonyl) chain (POAC chain) obtainable from two or more different linear hydroxycarboxylic acids or lactones thereof and a residue of an ethylenically unsaturated group wherein the amino and/or imino groups are attached via the ethylenically unsaturated group.

The POAC chain may be made from 2-hydroxyethylacrylate, ϵ-caprolactone and delta-valerolactone and the amine and/or imino groups may be provided by polyethylene imine. A polyester entity made from a monocarboxylic acid having at least two hydroxyl groups attached to the amino or imino group of the amine dispersant is not disclosed.

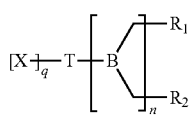
The above referenced publications claim the synthesis of a liquid polyethylene imine (PEI) based pigment dispersant by copolymerization of two or three different linear monomers. The backbone is PEI, and the grafting chain is a mixture-polyester, which is obtained by copolymerization of two or three different linear monomers, such as lactones, alkyl substituted lactones, and hydroxycarboxylic acids. Afterwards, these polyester chains are grafted onto PEI through both neutralization (forming salt bonds) and amidification (forming amide bonds) reactions between acid and amine groups.

Other Patent-Publications e.g. U.S. Pat. No. 6,395,804B1, U.S. Pat. No. 6,518,370B2 and U.S. Pat. No. 6,933,352B2 describe a dendritic dispersant based on a water-soluble dendritic polymer grafted with some hydrophobic groups. The hydrophobic groups were used as anchoring groups. Whereas the water-soluble dendritic polymer interacts with the water-soluble resin phase and builds up a steric environment to stabilize pigment dispersion. This kind of dispersants is not PEI-based, and used in water-based applications.

It has been found that an improved dispersant can be obtained by providing a polar poly-amine based dendritic dispersant.

The inventive products possess good storage stability, improved compatibility, and show lower viscosity of pigment concentrates, high gloss, less yellowing, and especially perfect dispersion effects for phthalocyanine pigments. In conclusion, generally the product of this invention provides a superior performance in alkyd, CAB, TPA, etc, paint system, compared to the prior art.

Thus, the invention relates to a dispersant of the formula I



wherein

T is selected from a polyethylene imine (PEI) or modified PEI moiety, polyvinylamine (PVA) or modified PVA, or polyallylamine (PAA) or modified PAA.

B is a branched monomer selected from a monofunctional carboxylic acid moiety having at least two hydroxyl groups or a monofunctional carboxylic acid moiety having at least two hydroxyl groups wherein one or more of the hydroxyl groups are hydroxyalkyl substituted,

R_1 and R_2 independently of one another are hydrophobic groups selected from a saturated or unsaturated fatty acid moiety with 3-24 carbon atoms, a monofunctional carboxylic acid moiety or a polymer moiety containing C_3-C_{24} alkyl (hydroxyl)carboxylic acid moieties with MW ranges from 100 to 10,000 g/mol,

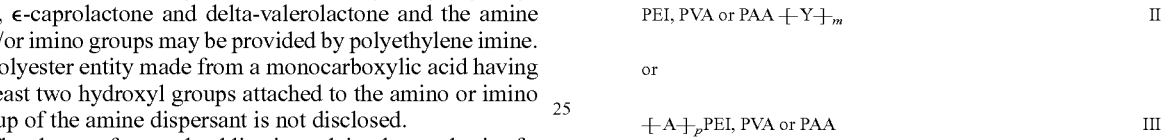
X is B with —OH terminal group, or R_1 or R_2,

q is a number between 5-2000, with the proviso that q is less than the sum of all amine groups of PEI, PVA, PAA.

n is a number of 1-6.

DEFINITIONS

The term modified PEI, modified PVA, and modified PAA is a group of formula II or III



wherein

Y is an extend monomer selected from a lactone, alkyl substituted lactone or a hydroxy carboxylic acid,

A is a side chain monomer selected from a monofunctional carboxylic acid containing 1-10 carbon atoms,

m is a number of 1-40,

p is a number of 1-1000, with the proviso that p is less than the sum of primary and secondary amine groups of the backbone PEI, PVA or PAA.

The term lactone refers to a cyclic ester produced by intramolecular condensation of a hydroxy acid with the elimination of water. It is preferably ϵ-caprolactone or valerolactone.

Alkyl substituted lactones are C_{1-6} alkyl lactones, preferably methylated caprolactones such as 4-methylcaprolactone, 3,5,5-trimethylcaprolactone, and 3,3,5-trimethylcaprolactone, 3-alkylvalerolactone and the like.

"Y" in Formula II may be a hydroxycarboxylic acid selected from glycolic acid, malic acid, lactic acid, hydroxyacrylic acid, alpha-hydroxybutyric acid, and the like; or a hydroxy-carboxylic acid derived from a lactone. Preferably Y is ϵ-caprolactone, valerolactone or an alkyl substituted lactone, more preferably ϵ-caprolactone or valerolactone.

The molecular weight of the extend moiety Y of preferably is in the range of 500-4,000 g/mol.

"A" in Formula III may be a monofunctional carboxylic acid selected from acetic acid, propionic acid, n-butyric acid, and the like.

"B" in formula I may be a monofunctional carboxylic acid having at least two hydroxyl groups selected from 2,2-bis (hydroxymethyl)propionic acid, α,α-bis(hydroxymethyl) butyric acid, α,α,α-tris(hydroxymethyl)acetic acid, α,α-bis-(hydroxymethyl) valeric acid, α,α-bis-(hydroxy) propionic acid, 3,5-dihydroxybenzoic acid, and the like.

More preferably B is 2,2-bis(hydroxymethyl)propionic acid, or α,α-bis(hydroxymethyl) butyric acid.

"R_1 and R_2" in formula I are preferably the same residues (R) and may be a monofunctional carboxylic acid selected from acetic acid, butyric acid, hexanoic acid, lauric acid, stearic acid, and the like; or hydroxystearic acid, ricinoleic acid, and various fatty acids.

"R_1 and R_2" in formula I may also be a polymer moiety containing alkyl(hydroxy)carboxylic acid moieties. Preferred is polyhydroxystearic acid (PHSA), with acid numbers of PHSA preferably between 10 and 200 mgKOH/g or acid terminated polyethers with molecular weight ranges from 200 to 5,000 g/mol.

More preferably "R_1 and R_2" are selected from lauric acid, stearic acid, polyhydroxystearic acid with an acid number of 20-200 mgKOH/g.

Preferences

In formula I q is preferably a number between 5-500 and n is preferably a number of 2-4.

In formula I, X is hydrophilic and is B with —OH termini if the mole ratio of R to B is less than $k''(k-1)/(k''-1)$. Whereas X is hydrophobic and is R if the mole ratio of R and B is above $k''(k-1)/(k''-1)$. "k" is the number of hydroxyl groups for B.

T is preferably polyethylene imine or modified polyethylene imine, more preferably polyethylene imine with MW ranging from 200-100,000 g/mol.

A in formula III is preferably acetic acid, propionic acid or n-butyric acid.

The modified ratio of primary and secondary amine groups for PEI with the side-chain monomers preferably is in the range of 25-75%.

Synthesis

Accessibility of the Starting Materials

PEI raw materials are commercial products from Nippon Shukubai etc. PVA raw materials are commercial products from Mitsubishi Kasei and PAA raw materials are commercial products from Nitto Boseki. Ethyl acetate, 2,2-bis(hydroxymethyl)propionic acid, fatty acids and lactones are commercial products.

Polyhydroxystearic acid can easily be prepared by methods known in the art.

To obtain a liquid form of a PEI-based dispersant, totally different from the "copolymerization" approach in prior arts, this invention focuses on introduction of "dendritic" moieties into the dispersant chemical structure via either convergent or disvergent approach.

"Dendritic" moiety means the moieties is synthesized via repeated reactions of branched monomers (containing at least one branch points, i.e. AB_2, or AB_3 type monomers, such as 2,2-bis(hydroxymethyl)propionic acid, α,α,α-tris(hydroxymethyl)acetic acid).

"Convergent" approach means a growth process which begins from what will become the surface of the dispersant and progresses radially in a molecular direction toward a focal point or core. The arm-dendritic moieties were synthesized via the (trans)esterification between branched monomer and hydrophobic moieties, and/or among branched monomers firstly. The obtained resultant progresses radially toward (modified) PEI in the analogous reaction. Through adjusting the ratio of branched monomer to hydrophobic moieties, the polarity and therefore the compatibility of the dendritic dispersant can be easily optimized.

"Disvergent" approach means a molecular growth process which occurs through a consecutive series of geometrically progressive step-wise additions of branches upon branches in a radially outward molecular direction to produce an ordered arrangement of layered branch generation, in which each macromolecule includes a core generation, one or more layers of internal generations, and an outer layer of surface generations, wherein each of the generations includes a single branched juncture. (Trans)esterification between (modified) PEI and branched monomer, and/or among branched monomers firstly, is operated as the step-wise addition of branched monomer into (modified) PEI. Then, hydrophobic moieties were grafted onto above resultant via esterification to adjust the polarity and therefore the compatibility of dendritic dispersant. Under optimized conditions, a liquid-form dispersant possessing of the storage stability, less-yellowing in white pigment formulations, especially good dispersion effect for blue pigment, low viscosity of pigment concentrates, performance of draw-downs and pour-outs in different let down systems is obtained.

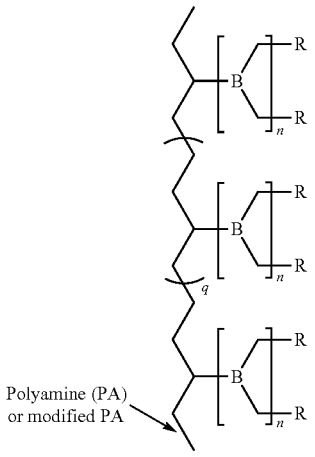
Thus, the invention relates to a process for the preparation of polyamine-based dendritic dispersants as represented in formula I by a "convergent" approach, characterized by (trans)esterification of B and R, or B and X to produce a dendritic arm firstly, and then grafting this arm onto core molecule T in sequence.

Or the invention relates to a process for the preparation of polyamine-based dendritic dispersants as represented in formula I by a "disvergent" approach, characterized by grafting B onto core molecule T firstly, then more and more B grafted onto the peripheral B of above obtained polymer layer by layer, finally, grafting R onto the above dendritic polymers.

The reaction temperatures range from 100° C. to 200° C., preferably 150° C. to 180° C. under N_2 atmosphere.

The products obtained have acid numbers of 5-25 mg KOH/g.

The products obtained are schematically shown below



B: is branched monomer R: is hydrophobic group, such as 2,2-bis(hydroxymethyl)proionic acid, such as lauric acid, stearic acid or α,α-bis(hydroxymethyl) butyric acid or polyhydroxystearic acid

EXAMPLES

Synthesis of Intermediate 1-4

Intermediate 1-4 were all prepared by the following process: 2,2-bis-(hydroxylmethyl)-propionic acid (BMPA, from Aldrich, MW 134), ϵ-caprolactone (CL, MW 114) 100.0 g, and di-butyltin dilaurate (DBTDL) ($5.0*10^{-4}$ w/w) were stirred under nitrogen and heated at 170° C. until solid contents reached 98%. Table 1 lists the results.

TABLE 1

Intermediate	CL:BMPA w/w	Product properties: Acid number mgKOH/g	Product properties: Appearance
1	1.7	150	Clear liquid
2	3.4	90	Clear liquid
3	5.1	65	Waxy solid
4	6.8	50	Solid

Intermediate 5-12

Intermediate 5-12 were all prepared by the following process: PEI (polyethylene imine)-EPOMIN® SP-200 (from Nippon Shokubai, MW 10,000), ϵ-caprolactone (CL) 100.0 g, and dibutyltin dilaurate (DBTDL) (5.0*10-.sup.4 w/w) were stirred under nitrogen and heated in a range of 170° C. for 1.0-30 h until solid contents reached 98%. Table 2 lists the results. In the case of Intermediate 7 and 9, the PEI was also replaced by EPOMIN® SP-018 (PEI, from Nippon Shokubai, MW 1,800). In the case of Intermediate 11 and 12, the PEI was re-placed by polyvinylamine (PVA200, from Mitsubishi Kasei, MW 10,000) and polyallylamine (PAA150, from Nitto Boseki, MW 10,000), respectively.

TABLE 2

Intermediate	CL:PEI w/w	Product properties: Amine number mgKOH/g	Product properties: Appearance
5	8.8	42	Clear liquid
6	26.3	14	Waxy solid
7	26.3	17	Solid
8	35.1	11	Solid
9	35.1	14	Solid
10	52.6	7.5	Solid
11	26.5	0.6	Solid
12	20.0	0.8	Solid

Intermediate 13

PEI, SP200 20 g and ethyl acetate 30 g were stirred and refluxed in a range of 90° C. until the solid content reached 55%. After removing the residuals under vacuum, the product was obtained as a viscous liquid with an amine number of 650 mg KOH/g.

Intermediate 14

This was prepared comparable to Intermediate 13, but refluxed until the solid content reached 60%. The product was obtained as a viscous liquid with an amine number of 430 mg KOH/g.

Intermediate 15

This was prepared comparable to Intermediate 13, but replaced SP200 by SP018. The product was obtained as a viscous liquid with an amine number of 660 mg KOH/g.

Intermediate 16

This was prepared comparable to Intermediate 13, but replaced SP200 by PAA150. The product was obtained as a waxy solid with an amine number of 360 mg KOH/g.

Intermediate 17

This was prepared comparable to Intermediate 14, but replaced SP200 by PVA200.

The product was obtained as a waxy solid with an amine number of 440 mg KOH/g.

Intermediate 18-20

Intermediate 18-20 were all prepared by the following process: 12-Hydroxystearic acid 100.0 g and DBTDL 0.10 g were stirred under nitrogen and heated in a range of 200° C. for 5-12 h. The by-product water was removed by refluxing with benzene. The products with different acid numbers were obtained according to different reaction times (Table 3).

TABLE 3

Intermediate	Reaction time h	acid number mgKOH/g	Appearance
18	5.0	95.4	Clear liquid
19	9.0	48.7	Clear liquid
20	12.0	29.6	Clear liquid

Examples Via "Convergent" Approach

Example 1

2,2-bis-(hydroxylmethyl)propionic acid (BMPA) 13.4 g and lauric acid 40.0 g were stirred under nitrogen and heated at 180° C. until acid number reduced as 115 mg KOH/g (1^{st} step). Then, EPOMIN® SP-200 (PEI) 12.9 g was added into the above resultant, stirred under nitrogen and heated at 180° C. until acid number reduced as 25.3 mg KOH/g (2^{nd} step). The product was obtained as a waxy solid with an amine number of 180 mg KOH/g.

Example 2-50

Example 2-50 were all prepared in a similar manner as Example 1 except that the amounts of precursors were varied as detailed in Table 4 below. Table 5 lists the results.

TABLE 4

Ex.	1^{st} step Precursors and its amount		Acid number in 1^{st} step mgKOH/g	2^{nd} step Precursor and its amount
2	13.4 g BMPA	22.8 g Lauric acid	24.8	1.8 g SP200
3	13.4 g BMPA	22.8 g Lauric acid	25.1	33.5 g Intermediate 8
4	13.4 g BMPA	22.8. g Lauric acid	24.9	5.5 g Intermediate 14
5	36.2 g Intermed. 1	40.0 g Lauric acid	81.2	12.9 g SP200
6	36.2 g Intermed. 1	40.0 g Lauric acid	80.5	177.5 g Intermediate 7
7	36.2 g Intermed. 1	40.0 g Lauric acid	79.2	17.1. g Intermediate 13
8	36.2 g Intermed. 1	22.8 g Lauric acid	15.5	25.4 g Intermediate 6

TABLE 4-continued

Ex.	1st step Precursors and its amount		Acid number in 1st step mgKOH/g	2nd step Precursor and its amount
9	59.0 g Intermed. 2	40.0 g Lauric acid	63.3	12.9 g SP018
10	59.0 g Intermed. 2	40.0 g Lauric acid	62.7	12.9 g SP200
11	59.0 g Intermed. 2	40.0 g Lauric acid	63.6	63.7 g Intermediate 5
12	59.0 g Intermed. 2	40.0 g Lauric acid	64	177.5 g Intermediate 6
13	59.0 g Intermed. 2	40.0 g Lauric acid	64.3	17.1 g Intermediate 15
14	59.0 g Intermed. 2	26.7 g Lauric acid	24.5	59.2 g Intermediate 6
15	59.0 g Intermed. 2	26.7 g Lauric acid	23.8	5.7 g Intermediate 13
16	59.0 g Intermed. 2	22.8 g Lauric acid	10.5	25.4 g Intermediate 6
17	59.0 g Intermed. 2	22.8 g Lauric acid	11.4	33.5 g Intermediate 8
18	59.0 g Intermed. 2	22.8 g Lauric acid	11.1	5.5 g Intermediate 14
19	59.0 g Intermed. 2	22.8 g Lauric acid	10.9	1.8 g SP200
20	59.0 g Intermed. 2	22.8 g Lauric acid	11.3	1.8 g SP018
21	59.0 g Intermed. 2	21.3 g Lauric acid	5.8	4.2 g Intermediate 5
22	59.0 g Intermed. 2	21.3 g Lauric acid	5.9	15.6 g Intermediate 9
23	59.0 g Intermed. 2	21.3 g Lauric acid	5.3	23.2 g Intermediate 10
24	59.0 g Intermed. 2	21.3 g Lauric acid	5.7	2.6 g Intermediate 14
25	81.8. g Intermed. 3	40.0 g Lauric acid	50.6	17.1 g Intermediate 15
26	81.8. g Intermed. 3	26.7 g Lauric acid	16.1	21.2 g Intermediate 5
27	81.8. g Intermed. 3	22.8 g Lauric acid	8.9	25.4 g Intermediate 7
28	81.8. g Intermed. 3	22.8 g Lauric acid	9.5	1.8 g SP 200
29	81.8. g Intermed. 3	22.8 g Lauric acid	9.2	5.5 g Intermediate 14
30	104.6 g Intermed. 4	40.0 g Lauric acid	40.6	12.9 g SP 018
31	104.6 g Intermed. 4	26.7 g Lauric acid	15.8	21.2 g Intermediate 5
32	104.6 g Intermed. 4	22.8 g Lauric acid	7.4	5.5 g Intermediate 14
33	13.4 g BMPA	32.4 g Stearic acid	24.6	33.5 g Intermediate 9
34	59.0 g Intermed. 2	32.4 g Stearic acid	10.1	33.5 g Intermediate 8
35	59.0 g Intermed. 2	32.4 g Stearic acid	9.8	5.5 g Intermediate 14
36	81.8 g Intermed. 3	32.4 g Stearic acid	8.1	25.4 g Intermediate 7
37	36.2 g Intermed. 1	67.2 g Intermed. 18	9.5	25.4 g Intermediate 6
38	59.0 g Intermed. 2	67.2 g Intermed. 18	7.4	33.5 g Intermediate 8
39	59.0 g Intermed. 2	131.0 g Intermed. 19	5.0	5.5 g Intermediate 14
40	81.8 g Intermed. 3	37.8 g Intermed. 20	13.6	1.7 g Intermediate 15
41	36.2 g Intermed. 1	22.8 g Lauric acid	15.5	25.4 g Intermediate 6
42	59.0 g Intermed. 2	22.8 g Lauric acid	10.5	25.4 g Intermediate 6
43	59.0 g Intermed. 2	22.8 g Lauric acid	10.9	1.8 g SP200
44	81.8 g Intermed. 3	26.7 g Lauric acid	16.1	21.2 g Intermediate 5
45	59.0 g Intermed. 2	22.8 g Lauric acid	10.9	0.6 g PVA200
46	59.0 g Intermed. 2	22.8 g Lauric acid	10.9	0.8 g PAA150
47	59.0 g Intermed. 2	22.8 g Lauric acid	10.9	16.8 g Intermediate 11
48	59.0 g Intermed. 2	22.8 g Lauric acid	10.9	17.0 g Intermediate 12
49	59.0 g Intermed. 2	22.8 g Lauric acid	10.9	2.2 g Intermediate 16
50	59.0 g Intermed. 2	22.8 g Lauric acid	10.9	1.8 g Intermediate 17

TABLE 5

Example	Acid number mgKOH/g	Amine number mgKOH/g	Appearance
2	5.1	46.3	Clear liquid
3	4.5	5.5	Waxy solid
4	4.7	41.8	Viscous liquid
5	15.2	135.3	Viscous liquid
6	14.5	11.5	Solid
7	16.3	71.5	Solid
8	3.6	4.5	Clear liquid
9	11.8	115.1	Waxy solid
10	10.7	108.4	Waxy solid
11	12.2	16.2	Waxy solid
12	11.2	8.8	Waxy solid
13	10.9	55.3	Waxy solid
14	4.6	5.5	Clear liquid
15	5.1	23.6	Clear liquid
16	3.5	3.6	Clear liquid
17	3.1	3.4	Viscous liquid
18	2.8	20.5	Clear liquid
19	3.0	19.8	Clear liquid
20	3.2	21.3	Clear liquid
21	2.0	2.6	Clear liquid
22	2.2	2.3	Clear liquid
23	2.5	1.9	Waxy solid
24	3.0	11.4	Clear liquid
25	11.2	49.5	Solid
26	4.0	6.8	Waxy solid

TABLE 5-continued

Example	Acid number mgKOH/g	Amine number mgKOH/g	Appearance
27	2.9	3.5	Viscous liquid
28	3.1	17.8	Clear liquid
29	2.9	17.1	Viscous liquid
30	7.9	79.6	Solid
31	3.5	6.2	Solid
32	2.3	14.2	Waxy Solid
33	5.5	4.5	Viscous liquid
34	3.1	3.2	Viscous liquid
35	2.9	18.9	Clear liquid
36	2.6	3.3	Viscous liquid
37	2.5	2.9	Clear liquid
38	2.4	3.0	Clear liquid
39	2.3	9.5	Clear liquid
40	2.7	14.2	Viscous liquid
41	7.8	4.6	Clear liquid
42	5.4	3.8	Clear liquid
43	5.1	22.5	Clear liquid
44	8.0	6.9	Waxy solid
45	4.5	6.5	Clear liquid
46	5.2	5.2	Clear liquid
47	4.6	0.3	Viscous liquid
48	5.0	0.4	Viscous liquid
49	5.4	4.2	Clear liquid
50	4.7	4.9	Clear liquid

Examples Via "Disvergent" Approach

Example 51

EPOMIN® SP200 (PEI) 12.9 g was stirred under nitrogen and heated at 180° C., and then 2,2-bis-(hydroxylmethyl) propionic acid (BMPA) 13.4 g was added step-wise. The above resultant was cooked at 180° C. until acid number reduced as 6.5 mgKOH/g (1st step). Then, lauric acid 40.0 g was added into the above resultant, stirred under nitrogen and heated at 180° C. until acid number reduced as 5.0 mgKOH/g (2nd step). The product was obtained as a waxy solid with an amine number of 85 mgKOH/g.

Example 52-102

Example 52-102 were all prepared in a similar manner as Example 51 except that the amounts of precursors were varied as detailed in Table 6 below. Table 7 lists the results.

TABLE 6

Example	1st step Precursors and its amount		Acid number of 1st step mgKOH/g	2nd step Precursor and its amount
52	SP018 6.5 g	Intermediate 2 59.0 g	6.7	Lauric acid 40.0 g
53	SP018 0.9 g	Intermediate 2 59.0 g	9.3	Lauric acid 16.0 g
54	SP 018 6.5 g	Intermediate 4 104.6 g	7.6	Lauric acid 40.0 g
55	SP200 0.9 g	BMPA 13.4 g	9.8	Lauric acid 16.0 g
56	SP200 6.5 g	Intermediate 1 36.2 g	6.2	Lauric acid 40.0 g
57	SP200 6.5 g	Intermediate 2 59.0 g	6.5	Lauric acid 40.0 g
58	SP200 0.9 g	Intermediate 2 59.0 g	9.9	Lauric acid 16.0 g
59	SP200 0.9 g	Intermediate 2 59.0 g	9.9	Lauric acid 12.0 g
60	SP 200 0.9 g	Intermediate 3 81.8 g	9.5	Lauric acid 16.0 g
61	Intermediate 5 63.7 g	Intermediate 2 59.0 g	6.6	Lauric acid 40.0 g
62	Intermediate 5 4.2 g	Intermediate 2 59.0 g	10.8	Lauric acid 14.9 g
63	Intermediate 5 21.2 g	Intermediate 3 81.8 g	8.9	Lauric acid 21.3 g
64	Intermediate 5 21.2 g	Intermediate 3 81.8 g	8.9	Lauric acid 16.0 g
65	Intermediate 5 21.2 g	Intermediate 4 104.6 g	8.8	Lauric acid 21.3 g
66	Intermediate 6 25.4 g	Intermediate 1 36.2 g	9.5	Lauric acid 16.0 g
67	Intermediate 6 177.5 g	Intermediate 2 59.0 g	7.1	Lauric acid 40.0 g
68	Intermediate 6 59.2 g	Intermediate 2 59.0 g	8.5	Lauric acid 21.3 g
69	Intermediate 6 25.4 g	Intermediate 2 59.0 g	9.7	Lauric acid 16.0 g
70	Intermediate 6 25.4 g	Intermediate 1 36.2 g	9.5	Intermediate 18 47.2 g
71	Intermediate 6 25.4 g	Intermediate 1 36.2 g	9.5	Lauric acid 12.0 g
72	Intermediate 6 25.4 g	Intermediate 2 59.0 g	9.7	Lauric acid 16.0 g
73	Intermediate 6 25.4 g	Intermediate 2 59.0 g	9.7	Lauric acid 12.0 g
74	Intermediate 6 25.4 g	Intermediate 2 59.0 g	9.7	Lauric acid 8.0 g
75	Intermediate 7 177.5 g	Intermediate 1 36.2 g	6.5	Lauric acid 40.0 g
76	Intermediate 7 25.4 g	Intermediate 3 81.8 g	9.5	Lauric acid 16.0 g
77	Intermediate 7 25.4 g	Intermediate 3 81.8 g	9.7	Stearic acid 22.7 g
78	Intermediate 8 33.5 g	BMPA 13.4 g	9.5	Lauric acid 16.0 g
79	Intermediate 8 33.5 g	Intermediate 2 59.0 g	9.4	Lauric acid 16.0 g
80	Intermediate 8 33.5 g	Intermediate 2 59.0 g	10.4	Stearic acid 22.7 g
81	Intermediate 8 33.5 g	Intermediate 2 59.0 g	8.9	Intermediate 18 47.2 g
82	Intermediate 9 15.6 g	Intermediate 2 59.0 g	10.9	Lauric acid 15.0 g

TABLE 6-continued

Example	1st step Precursors and its amount		Acid number of 1st step mgKOH/g	2nd step Precursor and its amount
83	Intermediate 9 33.5 g	BMPA 13.4 g	9.6	Stearic acid 22.7 g
84	Intermediate 10 23.2 g	Intermediate 2 59.0 g	10.3	Lauric acid 15.0 g
85	Intermediate 13 17.1 g	Intermediate 1 36.2 g	7.2	Lauric acid 40.0 g
86	Intermediate 13 5.7 g	Intermediate 2 59.0 g	8.8	Lauric acid 21.3 g
87	Intermediate 14 5.5 g	BMPA 13.4 g	9.9	Lauric acid 16.0 g
88	Intermediate 14 5.5 g	Intermediate 2 59.0 g	10.1	Lauric acid 16.0 g
89	Intermediate 14 2.6 g	Intermediate 2 59.0 g	10.7	Lauric acid 15.0 g
90	Intermediate 14 5.5 g	Intermediate 3 81.8 g	10.2	Lauric acid 16.0 g
91	Intermediate 14 5.5 g	Intermediate 4 104.6 g	9.4	Lauric acid 16.0 g
92	Intermediate 14 5.5 g	Intermediate 2 59.0 g	10.1	Stearic acid 22.7 g
93	Intermediate 14 5.5 g	Intermediate 2 59.0 g	10.0	Intermediate 19 91.7 g
94	Intermediate 15 17.1 g	Intermediate 2 59.0 g	7.3	Lauric acid 40.0 g
95	Intermediate 15 17.1 g	Intermediate 3 81.8 g	7.6	Lauric acid 40.0 g
96	Intermediate 15 1.7 g	Intermediate 3 8.18 g	7.6	Intermediate 20 37.8 g
97	PVA200 0.6 g	Intermediate 2 59.0 g	9.4	Lauric acid 16.0 g
98	PAA150 0.8 g	Intermediate 2 59.0 g	9.5	Lauric acid 16.0 g
99	Intermediate 11 16.8 g	Intermediate 2 59.0 g	10.2	Lauric acid 16.0 g
100	Intermediate 12 17.0 g	Intermediate 2 59.0 g	11.1	Lauric acid 16.0 g
101	Intermediate 16 2.2 g	Intermediate 2 59.0 g	9.1	Lauric acid 16.0 g
102	Intermediate 17 1.8 g	Intermediate 2 59.0 g	9.7	Lauric acid 16.0 g

TABLE 7

Example	Acid number mgKOH/g	Amine number mgKOH/g	Appearance
52	9.1	49.3	Waxy solid
53	4.5	8.5	Clear liquid
54	8.7	35.5	Solid
55	5.2	15.3	Clear liquid
56	8.5	34.5	Waxy solid
57	9.3	26.5	Waxy solid
58	5.6	5.5	Clear liquid
59	4.8	6.1	Clear liquid
60	5.7	4.2	Clear liquid
61	9.2	16.2	Waxy solid
62	5.2	2.4	Clear liquid
63	4.9	7.3	Waxy solid
64	4.6	8.0	Waxy solid
65	5.1	6.3	Solid
66	4.5	4.6	Clear liquid
67	10.1	8.4	Waxy solid
68	5.5	5.8	Clear liquid
69	5.2	3.6	Clear liquid
70	4.4	3.3	Clear liquid
71	4.7	4.9	Clear liquid
72	15.6	3.6	Clear liquid
73	6.0	3.8	Clear liquid
74	4.5	4.0	Clear liquid
75	9.8	11.5	Solid
76	6.0	3.5	Viscous liquid
77	5.5	3.3	Viscous liquid
78	4.5	5.8	Clear liquid

TABLE 7-continued

Example	Acid number mgKOH/g	Amine number mgKOH/g	Appearance
79	5.2	3.4	Clear liquid
80	4.9	3.3	Clear liquid
81	6.2	3.0	Clear liquid
82	5.3	2.9	Clear liquid
83	4.5	6.7	Viscous liquid
84	4.9	2.1	Waxy solid
85	10.5	60.6	Solid
86	6.0	22.7	Clear liquid
87	5.2	47.2	Clear liquid
88	4.5	18.5	Clear liquid
89	6.0	10.3	Clear liquid
90	5.3	15.2	Viscous liquid
91	6.2	12.2	Waxy solid
92	4.9	16.9	Clear liquid
93	8.3	10.2	Viscous liquid
94	11.3	48.7	Waxy solid
95	10.7	40.8	Solid
96	12.5	12.0	Solid
97	5.1	0.3	Clear liquid
98	4.7	0.2	Clear liquid
99	5.6	0.1	Viscous liquid
100	4.3	0.2	Viscous liquid
101	5.0	0.4	Clear liquid
102	4.8	0.3	Clear liquid

Performance Screening

In order to test the dispersion effect of the obtained samples, Resin Free Pigment Concentrates were prepared according to the Formulation 1. The mill base was dispersed in Scandex Shaker for 1.5 h with the help of glass beads. Afterwards the mill base was filtered and stored at room temperature overnight. Let-downs (Formulation 2) for testing were based on a stoving enamel, and a CAB base coat. Formulation 3 shows the paint formulations for the stoving enamel and CAB paints. The paint preparation was mixed under high speed stirring for 5 minutes at 2000 rpm, and applied on polyester film with a 35-75 μm film thickness. After preparing draw-downs, the rest of paints were diluted 1:1 with butyl acetate for a pour-out test.

First, the competitive grades were synthesized according to patents, e.g. WO 9421368, U.S. Pat. No. 5,700,395, U.S. Pat. No. 6,583,213, and U.S. Pat. No. 6,599,947 and so on. The performance of these grades was tested according to Formulations 1, 2, and 3. Results showed competitive product A performs better than the others, which was then taken as a representative dispersant in the text.

Formulations 1. Preparation of Pigment Concentrates

		Pigment Concentrate No.			
	Ingredients	1	2	3	4
1)	Dispersant (100% solid)	5.35	6.00	3.62	3.25
2)	1-methoxy-2-propyl acetate (MPA)	19.65	25.62	31.38	21.7
3)	Pigment White 21	75.00			
4)	Pigment Black 7 (Special Black 100)		20.00		
5)	Pigment Blue 15:2			15.00	
6)	Pigment Red 254				25.00
7)	3.0 mm glass beads	100.0	100.0	100.0	100.0
	Total (g)	200.0	150.0	150.0	150.0

Formulations 2. Let-Down Systems

a) Stoving Enamel	VIALKYD ® AC 451	68.4
	Maprenal MF 650	31.4
	Ciba ®EFKA ®3030	0.2
	Total	100
b) CAB base coat	CAB 531-1	11.2
	Butyl acetate	51.9
	URACRON ® CR 226 XB	32.1
	Uramex MF 821	4.8
	Total	100.0

VIALKYD® AC 451 is an alkyd resin.

Maprenal MF 650: melamine resin, Degussa.

Ciba ®EFKA ®3030 is a modified polysiloxane solution slip and leveling agent.

CAB-531 cellulose acetate butyrate material commercially available from Eastman Chemical.

Uracron CR 226 XB. DSM Coating Resins Uracron CR, OH acrylic.

Uramex MF 821: DSM Coating Resins Uramex (amino).

VIALKYD® AC 451 is an alkyd resin,

Maprenal MF 650: melamine resin, Degussa,

Ciba®3030 is a modified polysiloxane solution slip and leveling agent,

CAB-531 cellulose acetate butyrate material commercially available from Eastman Chemical,

Uracron CR 226 XB. DSM Coating Resins Uracron CR, OH acrylic,

Uramex MF 821: DSM Coating Resins Uramex (amino).

Formulation 3. Cab and Stoving Enamel Paints

Code	1	2	3
Let-down (formulation 2a or 2b)	9.0	7.5	7.0
PC white (No. 2 in Formulation 1)	—	2.0	3.0
PC color (No. 4-6 in Formulation 1)	1.0	0.5	—
Total/g	10.0	10.0	10.0

The performance of examples 1-102 in Table 5 and 7 were tested according to Formulations 1, 2 and 3. It was observed, that the pigment concentrates flow well and their viscosities were comparable or lower than the competitive product A. The rheological behavior of the pigment concentrates was measured with a Thermo-Haake RheoStress 600 equipment under the CR mode. The initial viscosities (η_0) and dynamic viscosities (η_t) of the pigment concentrations are listed in Table 8. According to the viscosity curves, the Pigment White concentrates (PW 21) have a Newtonian flow, while the Pigment Black concentrates (Special Black-100) exhibit a pseudoplastic flow. The Pigment Blue concentrates (PB 15:2) have plastic flows and thixotropic properties, but could easily flow under a low shear stress (i, in Table 8). In general, some examples were taken as the representative dispersants, such as 16-19, 46, 50, 58, 69, 79, 88, 97, and so on.

TABLE 8

Rheological data of Pigment Concentrates

	PW 21		Special Black 100		PB 15:2	
Example	η_0 mPas	η_t mPas	η_0 mPas	η_t mPas	τ/Pa (at Yield point)	η_t mPas
Competitive product A	1000	360	>1000	300	50	150
16	450	200	600	150	28	80
19	330	170	550	140	20	70
62	550	240	480	120	30	80
69	780	350	430	130	25	80
79	650	310	450	100	18	60
89	710	340	400	140	20	70

Competitive product A is prepared according to U.S. Pat. No. 6,583,213, Ex. 9.

In the stoving enamel paint, the CAB paint, the performance of the dispersants was generally very good with satisfactory results, e.g. high gloss (on average, above 80 at 20°), no seeding, no rub-out, good color strength, and less yellowing of the white pigment (Table 9). Especially, the dispersants provided the better dispersant effect for blue pigment compared with the competitive products, even in TPA paint system (Formulation 4) as listed in Table 10

TABLE 9

The Yellowness and Whiteness of draw downs.

	Stoving		CAB	
Example	Yellowness	Whiteness	Yellowness	Whiteness
Competitive product A	2.5	80	−0.8	88
16	1.45	84	−0.69	86
18	1.50	85	−0.74	88
58	0.56	89	−0.59	88
62	0.69	86	−0.65	90
72	0.54	87	−0.60	88
88	0.60	88	−0.68	89

Measured by X-rite MA 68II multi-angle spectrophotometer at 45° according to criterion ASTM E313.

Formulations 4. TPA Paint System

TPA base coat	PARALOID™ B-66, thermoplastic acrylate, Rohm Haas	40
	Xylene	8.0
	Toluene	38
	MPA	13.5
	Ciba ®EFKA ®3030	0.5
	Total	100.0

Ciba ®EFKA ®3030 is a modified polysiloxane solution slip and leveling agent

TABLE 10

The dispersion effect for Pigment Blue 15:2 in TPA paint system

Example	Gloss of drawdown 20/60°	Seeding	Gloss of pour out 20/60°
Competitive product A	60/80	Many seeding	42/77
16	81/88	no seeding	58/86
18	79/84	few seeding	54/84
58	81/86	no seeding	56/85
62	82/87	no seeding	59/86
72	80/84	few seeding	55/84
88	83/89	no seeding	60/88

In the solubility test, samples were dissolved in various solvents first with a concentration of 50% (w/w), and then keep for one month at 25° C. and −5° C., respectively. Obviously, the dispersants of this invention provided an improved solubility compared with competitive products (Table 11). It indicates that the invention samples are less crystallization, and their compatibility in various solvent systems is better than that of the competitive product A.

TABLE 11

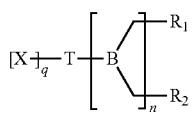
Solubility of samples in various solvent (50%, w/w)

	MPA		n-butyl acetate		2-Butanone		Xylene	
Example	25° C.	−5° C.	25° C.	−5° C.	25° C.	−5° C.	25° C.	−5° C.
Product A	✓x*	x*	✓x	x	✓	✓x	✓	✓x
17	✓*	✓x	✓	✓x	✓	✓	✓	✓
18	✓	✓	✓	✓	✓	✓	✓	✓
58	✓	✓	✓	✓	✓	✓	✓	✓
72	✓	✓	✓	✓	✓	✓	✓	✓
83	✓	✓x	✓	✓x	✓	✓	✓	✓
88	✓	✓	✓	✓	✓	✓	✓	✓

*✓: solubility is good, and the solution is clear;
✓x: solubility is medium and partially crystallized;
x: solubility is poor and totally crystallized.

The invention claimed is:

1. A dispersant of formula I



I

wherein

T is selected from polyethylene imine (PEI), modified PEI, polyvinylamine (PVA), modified PVA, polyallylamine (PAA) and modified PAA moieties, wherein the modified PEI, modified PVA, and modified PAA is a group of formula II or III

II

or

III,

wherein Y is an extend monomer selected from a lactone, alkyl substituted lactone or a hydroxyl carboxylic acid, A is a side chain monomer selected from a monofunctional carboxylic acid containing 1-10 carbon atoms, m is a number of 1-40, p is a number of 1-1000, with the proviso that p is less than the sum of primary and secondary amine groups of the backbone PEI, PVA or PAA,

B is 2.2-bis(hydroxymethyl)propionic acid or α,α-bis(hydroxymethyl) butyric acid,

R_1 and R_2 are identical and are selected from lauric acid and stearic acid,

X is B with —OH terminal group, R_1, or R_2,

q is a number between 5-2000, with the proviso that q is less than the sum of all amine groups of PEI, PVA or PAA,

n is a number of 1-6,

wherein the dispersant of formula I is made by a "convergent" or "disvergent" approach,

wherein the "convergent" approach is characterized by reaction of

B and R_1 or R_2, or

B and X

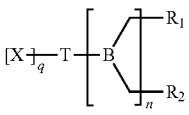
to produce an arm firstly, and then grafting this arm onto core molecule T in sequence,

wherein the "disvergent" approach is characterized by grafting B onto core molecule T firstly, then more and more B grafted onto the peripheral B of above obtained polymer layer by layer, finally, grafting R_1 and/or R_2 onto the above polymers.

2. The dispersant according to claim **1** wherein T is polyethylene imine or modified polyethylene imine.

3. The dispersant according to claim **1** wherein Y is ϵ-caprolactone or valerolactone.

4. A process for preparation of a polyamine-based dispersant of formula I



I

wherein

T is selected from polyethylene imine (PEI), modified PEI, polyvinylamine (PVA), modified PVA, polyallylamine (PAA) and modified PAA moieties, wherein the modified PEI, modified PVA, and modified PAA is a group of formula II or III

II

or

III,

wherein Y is an extend monomer selected from a lactone, alkyl substituted lactone or a hydroxylcarboxylic

acid, A is a side chain monomer selected from a monofunctional carboxylic acid containing 1-10 carbon atoms, m is a number of 1-40, p is a number of 1-1000, with the proviso that p is less than the sum of primary and secondary amine groups of the backbone PEI, PVA or PAA,

B is 2.2-bis(hydroxymethyl)propionic acid or α,α-bis(hydroxymethyl) butyric acid,

R_1 and R_2 are identical and are selected from lauric acid and stearic acid,

X is B with —OH terminal group, R_1 or R_2

q is a number between 5-2000, with the proviso that q is less than the sum of all amine groups of PEI, PVA or PAA,

n is a number of 1-6,

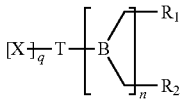
by a "convergent" approach, characterized by reaction of B and R_1 or R_2, or B and X

to produce an arm firstly, and then grafting this arm onto core molecule T in sequence.

5. The process according to claim **4** whereby the reaction temperatures range from 100° C. to 200° C. under N_2 atmosphere.

6. The process according to claim **5** wherein the products obtained have acid numbers of 5-25 mgKOH/g.

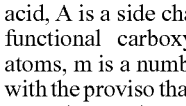
7. A process for preparation of a polyamine-based dispersant of formula I



I

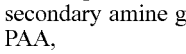
wherein

T is selected from polyethylene imine (PEI), modified PEI, polyvinylamine (PVA), modified PVA, polyallylamine (PAA) and modified PAA moieties, wherein the modified PEI, modified PVA, and modified PAA is a group of formula II or III



II

or



III,

wherein Y is an extend monomer selected from a lactone, alkyl substituted lactone or a hydroxylcarboxylic acid, A is a side chain monomer selected from a monofunctional carboxylic acid containing 1-10 carbon atoms, m is a number of 1-40, p is a number of 1-1000, with the proviso that p is less than the sum of primary and secondary amine groups of the backbone PEI, PVA or PAA,

B is a branched monomer selected from a monofunctional carboxylic acid moiety having at least two hydroxyl groups and a monofunctional carboxylic acid moiety having at least two hydroxyl groups wherein one or more of the hydroxyl groups are hydroxyalkyl substituted,

R_1 and R_2 independently of one another are hydrophobic groups selected from a saturated or unsaturated fatty acid moiety with 3-24 carbon atoms, a monofunctional carboxylic acid moiety or a polymer moiety containing C_3-C_{24} alkyl (hydroxyl)carboxylic acid moieties with MW ranges from 100 to 10,000 g/mol,

X is B with —OH terminal group, R_1 or R_2

q is a number between 5-2000, with the proviso that q is less than the sum of all amine groups of PEI, PVA or PAA,

n is a number of 1-6,

by a "disvergent" approach, characterized by grafting B onto core molecule T firstly, then more and more B grafted onto the peripheral B of above obtained polymer layer by layer, finally, grafting R_1 and/or R_2 onto the above polymers.

8. The process according to claim **7** whereby the reaction temperatures range from 100° C. to 200° C., preferably 150° C. to 180° C. under N_2 atmosphere.

9. The process according to claim **8** wherein the products obtained have acid numbers of 5-25 mgKOH/g.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 9,381,481 B2
APPLICATION NO. : 12/442142
DATED : July 5, 2016
INVENTOR(S) : Huiguang Kou et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In the Claims:

At Column 16, line 18, "B is 2.2-bis" should be -- B is 2,2-bis --.

At Column 16, line 67, "hydroxylcarboxylic" should be -- hydroxyl carboxylic --.

At Column 17, line 7, "B is 2.2-bis" should be -- B is 2,2-bis --.

At Column 17, line 10, "R_1 or R_2" should be -- R_1, or R_2, --.

At Column 18, line 8, "hydroxylcarboxylic" should be -- hydroxyl carboxylic --.

At Column 18, line 26, "R1 or R2" should be -- R1, or R2, --.

Signed and Sealed this
Twenty-ninth Day of November, 2016

Michelle K. Lee

Michelle K. Lee
Director of the United States Patent and Trademark Office